Background and Basics

- AFFF Developed in the early 1960’s by NRL and 3M
- Hydrocarbon foaming agents
- Fluorinated surfactant
- MilSpec requires the use of a fluorinated surfactant and other compounds as required to conform to the specification

The Need for AFFF

- Many applications worldwide depend on the capabilities of the US military developed AFFF

- While many worldwide applications may be satisfied with reduced-performance products, the US military performance requirements cannot be reduced without potential loss of life and platform survivability

AFFF Capabilities

- No other agent can equal its ability to rapidly extinguish a pool fire
- Does not require an aspirating nozzle
- Vital to confronting:
  – Potential ordinance cook-off
  – Pool fires threatening aircraft crew
  – Threat to concentrated high value assets

Drop-In vs. Substitute

- True drop-in: uses current equipment (tanks, proportioners, piping, nozzles)
- Substitute: need to replace or modify existing shipboard delivery systems
- Navy ships built around existing AFFF systems performance envelope
- Not fea$ible to modify current systems
  - Downtime, in addition to space, weight, cost
- New platforms have more flexibility, but need to maintain compatibility, interchangeability

AFFF Performance

- Prevents radiation from reaching fuel
- Retards pyrolyzates and fuel from reaching flame
- Absorbs heat
- Cools fuel
- Rapidly spreads, covers and reseals fuel surface


AFFF Properties

- Surface Tension
- Viscosity
- Foam quality
  - Drainage
  - Thermal stability
- Film fire protection

AFFF: Science and Specifications

- What AFFF properties contribute to fire suppression?
- How can these characteristics best be specified?
- What is not necessary?
- How can we achieve a better product?

Understanding Aqueous Film Forming Foam

- Simplistic model uses two interacting fluids
  - AFFF is less dense and more viscous
  - Use oil over water principles
- Simplistic model does not accurately determine spreading
- Reality: non-Newtonian behavior greatly complicates modeling
- Surfactant diffusion, adsorption, and solubility further complicates modeling

Surface Tension

- AFFF reduces surface tension of water from 70 dyn/cm to approximately 15-20 dyn/cm
- Hydrocarbon surface tensions range from 20-30 dyn/cm
- Need desired balance between surface tensions for AFFF to exist and spread
  - Fuel
  - Interfacial Region
  - AFFF

Spreading Coefficient

- Thermodynamic measure of one liquids ability to flow on another liquid
- Spreading Coefficient = $\gamma_{fuel} - \gamma_{AFFF} - \sigma_{fuel\text{-}AFFF}$
- The spreading coefficient is a thermodynamic value: Can the action occur?
  - Very easy to measure, but …
- Should determine a kinetic spreading coefficient: Will the action occur and will it be fast enough?

Spreading Coefficient – Surface Tension

- Dynamic surface tensions, as opposed to equilibrium spreading parameters, control spreading. The rate of interfacial and surface tension reduction drives spreading.

- Data exists for systems that do **not** exhibit spreading, yet possess positive equilibrium spreading coefficients.

Viscosity

- Affects concentrate flow, proportioning and foam characteristics
- Is a specific viscosity range required?
- Is a reproducible range needed for proportioning?
- Concentrate bulk viscosity is specified but foam **dynamic** surface viscosity controls foam characteristics

Fire Performance Evaluation

- Number of attempts to achieve success should be limited
- Some degree of test automation would help remove some operator variation factors
- Range of concentrations should be evaluated, but ½-strength test supplies safety margin for extrapolating to untested threat scenarios
- Standardized fuel vs. variable (gasoline)

Mil-F-Spec 24385F Chemical and Physical Specifications

- Viscosity
- Refractive Index
- Fluorine Content
- pH
- Total Halides
- Corrosion- General and Localized
- Stability
- Compatibility
- Dry Chemical Compatibility
- Film Formation and Sealability
- Spreading Coefficient
- Foamability
- Biological Oxygen Demand/ Chemical Oxygen Demand
- Toxicity

Refractive Index

- Field/shipboard measure of AFFF concentration
- Conductivity alternative field technique but NFPA cautions against use for sea water applications
- What has to be done to achieve MilSpec refractive index?
  - Added constituents
  - Negative effect on AFFF performance?
  - Ease MilSpec refractive index requirement?
- Other options for concentration determination (e.g., colorimetric)

Fluorine Content

- Metric for batch-to-batch quality control
- Methodology not specified in MilSpec rev. F
- Should fluorine or surfactant concentration be determined?
- Other methodologies for quality control

Corrosivity

- pH, general corrosion, localized corrosion
- Total Halides
  - Free halides promote metallic corrosion
  - “Total” is misleading
    - Method more applicable to determining “free” chloride and bromide
    - Method likely does not measure fluoride
- Sulfur and heavy metals not in Mil-Spec

Stability and Compatibility

- Stability Requirement
  - 10 day storage at elevated temperature neither physically degrades AFFF nor diminishes selected performance criteria
  - Should halide content (specifically fluoride from fluorosurfactant decomposition) also be considered?
- Compatibility Requirement
  - Mix candidate AFFF with approved AFFF and submit to stability test
  - MilSpec rev. F nebulous regarding number of mixtures with approved AFFF to use and ratios
  - Long term implications of new technologies

Toxicity

- Killifish toxicity a measure of short-term toxicity for salt water fish
- Killifish toxicity more difficult test relative to fresh water fish toxicity, but Navy concerned with salt water
- AFFFs historically considered relatively non-toxic
- Persistent, Bioaccumulative and Toxic components
- Telomer/PFOA issues – may jeopardize remaining AFFFs on the QPL list

Operational Restrictions

- Limitations already exist
- More stringent regulations are in the pipeline (UNDS)
- New AFFF formulations and MilSpec modifications need to anticipate impact of future regulations

AFFF Chemical and Physical Specifications from Other Organizations

- UL 162
  - Spreading coefficient
  - Foam Quality
  - Concentration (RI or conductivity)
- ISO 7203-1
  - Sediment size and quantity
  - Comparative fluidity
  - pH
  - Surface Tension, Interfacial Surface tension, Spreading Coefficient
  - Foam Quality
- ISO stability testing more stringent, but UL / ISO fire protection performance tests less challenging

Conclusions

- AFFF is a fast and efficient way to extinguish two-dimensional hydrocarbon fires.
- Evaluation of new products to the existing specification is ongoing.
- If a new AFFF is required, a drop-in is the goal.
- Improved understanding of AFFF action will lead to design of less environmentally threatening products. Opportunity for DoD-Industry cooperation for mutual benefit.

Future Directions

- Modification of the Military Specification, where feasible without compromising fire protection performance, will expand possible AFFF formulation options.

- Government - industry interactions can help formulate possible modifications to MIL-F-24385F.